Thermally stable carbon-related centers in 6H-SiC: photoluminescence spectra and microscopic models

Alexander Mattausch,[*] Michel Bockstedte, and Oleg Pankratov

Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, 91058 Erlangen, Germany

John W. Steeds,[†] Suzanne Furkert, Jonathan M. Hayes, and Wayne Sullivan

Department of Physics, University of Bristol, BS8 1TL Bristol, UK

Nick G. Wright

Department of Electrical, Electronic & Computer Engineering, University of Newcastle, UK

(Dated: February 5, 2008)

Recent *ab initio* calculations [Mattausch *et al.*, Phys. Rev. B **70**, 235211 (2004)] of carbon clusters in SiC reveal a possible connection between the tricarbon antisite $(C_3)_{Si}$ and the U photoluminescence center in 6H-SiC [Evans *et al.*, Phys. Rev. B **66**, 35204 (2002)]. Yet, some of the predicted vibrational modes were not observed experimentally. Here we report experiments which indeed confirm the existence of a low-energy mode for the U-center (as well as for the HT3- and HT4-centers with spectral details similar to the U-center). We calculated the isotope splitting for the $(C_3)_{Si}$-defect and found near-perfect agreement with our data. In addition, we discuss the carbon di-interstitial $(C_2)_{Hex}$ as a model for the Z- and HT5-centers. The isotope splitting is also well reproduced, but the absolute values of the local mode energies show a discrepancy of about 10 meV.

Silicon carbide (SiC) is a wide band-gap semiconductor especially suitable for high-power, high-temperature and high-current applications. Due to its extreme hardness and low diffusion coefficients, the method of choice for the creation of the doping profiles is ion implantation. However, implantation causes a severe damage of the crystal and a subsequent annealing at high temperatures is necessary to eliminate the defects—mostly vacancies and interstitials. Unfortunately, not all interstitials and vacancies recombine. They can also cluster and form thermally stable aggregates. One example is the well-known D_{II}-center,[1] which is most likely an aggregation of carbon atoms around carbon antisites.[2,3,4]

Recent photoluminescence (PL) measurements[5] of electron-irradiated 6H-SiC have shown that besides the D_{II}-center other intrinsic defect centers exist which also possess localized vibrational modes (LVM's) above the SiC bulk phonon energy. These are the P−T centers, which were tentatively assigned to carbon split-interstitials or di-carbon antisites,[3,4] and the U-center, for which a single LVM at nearly 250 meV was observed. The three-fold isotope splitting in ^{13}C-enriched samples signifies a carbon-related defect, although carbon-based defects with such a high vibrational frequency have not been known in SiC. Yet, *ab initio* calculations predict[3] that such defects may exist. Namely the tri-carbon antisite $(C_3)_{Si}$ has several LVM's up to 250 meV. The energetically highest mode even reproduces the three-fold isotope splitting of the U-center. However, the missing phonon replicas in available PL spectra could not be explained in Ref. 3. Yet, the clear identification of observed carbon-related defect centers is important since it may substantiate the carbon aggregation phenomenon in SiC predicted by earlier theoretical work.[2,3,4] Besides, at elevated temperatures these aggregates can re-emit carbon-interstitials[6] and thereby facilitate the formation of further defect centers like D_I or the alphabet-lines.[7]

In this paper we present photoluminescence results for ^{13}C-enriched 6H-SiC samples and compare them with *ab initio* calculations. The data show an additional phonon replica of the U-center at 150 meV, which is in agreement with the calculated LVM of $(C_3)_{Si}$. Further centers, which are similar to the U-center and labeled HT3 and HT4, were also observed. With this new experimental data in hand, the centers are well explained by the tri-carbon antisite $(C_3)_{Si}$ model. The centers Z and HT5 are also discussed. These centers possess two vibrational modes above the SiC bulk phonon spectrum at about 170 meV and 200 meV and also exhibit a three-fold isotope splitting of the energetically highest mode. Their relationship with the carbon di-interstitials is discussed. We show that a three-fold isotope splitting with the frequency ratios of a C−C dumbbell (which is the square root of the mass ratios), does not necessarily originate from a dumbbell-shaped defect. Both the tri-carbon antisite and the carbon di-interstitial represent complex defect configurations.

In the following, we first present the experimental details and results and then turn to the theoretical calculations. Theoretical results are then compared with the experimental data.

The investigated samples were n- and p-type 6H-SiC with typical doping levels in the range $10^{15}-10^{16}$ cm^{-3}. They included both epitaxially grown layers and Lely grown crystals. The p-type specimens showed strong donor-acceptor pair-luminescence. To produce the defect centers the samples were electron irradiated with electron energies below and above the silicon displace-

TABLE I: ZPL's and LVM's of the centers in 6H-SiC.

center	ZPL (nm)	ZPL (eV)	LVM1 (meV)	LVM2 (meV)
Z	512.5	2.417	171.6	202.0
HT5	509.8	2.431	169.0	201.7
HT3	492.9	2.515	151.0	246.3
U	525.0	2.361	151.6	246.6
HT4	546.4	2.268	149.9	244.7

ment threshold at about 250 keV. The irradiation was performed using an ion-free transmission electron microscope. To allow for an identification of the defects via the isotope splitting of the phonon replicas, samples with a ^{13}C enrichment of 30% were used in addition to the samples with natural isotope abundance. For the PL measurements the samples were cooled to 7 K using Oxford Instruments microstats on Renishaw microRaman spectrometers. The centers were excited using laser wavelengths of 325 nm and 488 nm.

The reported centers were produced by high-temperature anneals in the range 1000−1500°C. The U- and the Z-center came up at the lower end of this range and persisted in some cases up to 1500°C. The centers HT3 and HT4 were observed after 1200°C and 1300°C anneals, respectively. While HT3 was always present, HT4 appeared only in some samples. The HT5-center was observed after the highest temperature of 1500°C.

All of the optical transitions were excited by both the 325 nm and the 488 nm wavelength. A major effort was put into the deconvolution of the observed spectra, since considerable overlap occurred between the spectral details. Employing three different techniques we were able to unambiguously assign the spectral details to a specific zero phonon line (ZPL). One method was by spatial separation. Spectra were obtained at a series of points along lines through the irradiated region, and the relative intensities of the ZPL's changed with position. A second approach was the comparison of the results after different annealing temperatures, which also affected the relative intensities of the spectra. The third method was the investigation of a wide range of specimens irradiated with different electron doses and energies. Further details on this approach can be found in Refs. 5 and 8.

Figure 1a shows the PL spectra of the U- and the Z-centers in ^{13}C-enriched 6H-SiC. Both centers were originally discussed in Ref. 5. The three-fold isotope splitting of the high-energy mode at 246.6 meV is clearly visible. In addition to the single originally observed mode[5] a further mode with a lower energy was observed at 151.6 meV in samples with natural C abundance (cf. Table I). In isotope-enriched SiC this mode splits in a complex fashion (cf. Fig. 1a). The centers HT3 and HT4 possess properties similar to those of the U-center. Figure 1b shows the HT3-center alongside the Z-center in ^{13}C-enriched 6H-SiC. Each center also has a high-energy mode around 245 meV (cf. Table I) exhibiting a three-fold isotope split-

ting (cf. inset of Fig. 1b for HT3) and a lower-energy mode around 150 meV. Some aspects of the HT3- and HT4-centers deserve particular mention. First, in the sample with natural C-abundance the high-energy mode coincides with the ZPL of HT4 at 546 nm (cf. Fig. 1c). Clear evidence of a LVM at this wavelength could be deduced from a ^{13}C-enriched sample which lacks the HT4-luminescence and shows a clear three-fold isotope splitting. The second aspect is the small separation between the lower-energy mode of HT3 and the ZPL of the U-center (cf. Fig. 1c). Although the LVM could be clearly identified in the sample with natural C-abundance, the isotope splitting could not be deduced.

The Z-center is clearly present in all shown spectra. Its full details are visible in Fig. 1b. It possesses 4 LVM's, yet only two of them (Z_C and Z_D in Fig. 1b) are above the SiC bulk phonon spectrum at 172 meV and 202 meV. The HT5-center possesses similar properties (cf. Table I). In ^{13}C-enriched samples the high-energy mode shows a three-fold isotope splitting, while the lower-energy mode exhibits a complex broadening (cf. Fig. 1b).

The high vibrational energy and the three-fold splitting of the highest mode upon carbon isotope substitution suggest that the observed defect centers are carbon-related. Hence we focused our theoretical modeling on carbon-interstitial and carbon-antisite complexes. We employed density-functional theory with the local density approximation (LDA) as implemented in the software package FHI96SPIN.[9] Supercells with 216 sites for 3C-SiC and 128 sites for 4H-SiC and a plane wave basis set with a cut-off energy of 30 Ry were used. The Brillouin zone was sampled by a single Γ-point for the large 3C-SiC supercells. For 4H-SiC a $2 \times 2 \times 2$ Monkhorst-Pack mesh[10] was used except for the calculation of the LVM's, where we used only the Γ-point. Due to the large supercells the defect molecule approximation was employed for the analysis of the LVM's. In this approach the calculation of the dynamical matrix is restricted to the defect and its nearest-neighbor atoms (cf. Ref. 3 for details). We verified that this approximation affects only the lowest-energy LVM's close to the bulk phonon band.[2]

The candidates for the centers described above must possess two properties: they must exhibit a three-fold isotope splitting of the highest mode in ^{13}C-enriched material and they must be thermally stable. Two possibilities are the carbon di-interstitial $(C_2)_{Hex}$ and its structurally similar configurations in 4H-SiC and the tri-carbon antisite $(C_3)_{Si}$. The calculations were performed for 3C- and 4H-SiC. A close agreement of the results for the two polytypes ensures the transferability to the more complex 6H-SiC. The defects are depicted in Fig. 2 for 3C-SiC. The thermal stability is guaranteed by high dissociation energies, which are 4.8 eV (5.8 eV) for $(C_3)_{Si}$ in 3C-SiC (4H-SiC) and 4.8 eV for $(C_2)_{Hex}$ in 3C-SiC. In 4H-SiC, various configurations exist for the di-interstitial with dissociation energies between 5.1 eV and 5.5 eV. The most stable defect is $(C_{sp})_{2,hh}$ with two carbon split-interstitials at neighbouring sites. The interstitial carbon atoms relax
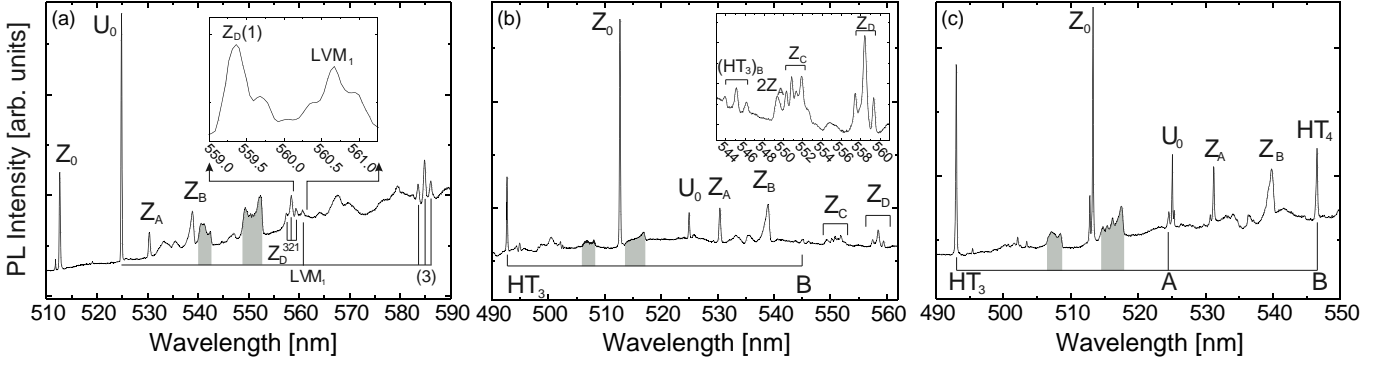
FIG. 1: Spectra of 6H-SiC samples (taken at $T = 7\,\mathrm{K}$ with a laser wavelength of $325\,\mathrm{nm}$) with a ^{13}C-enrichment of 30% and natural isotope abundance showing the U-, Z-, HT3- and HT4-centers. The shaded regions indicate the bulk phonons belonging to the marked ZPL. (a) The U- and the Z-center in a ^{13}C-enriched sample. The inset displays the broadened lower-energy mode of the U-center and the ^{12}C$-^{12}$C-peak of the energetically highest Z-mode. (b) The HT3- and the Z-center in a ^{13}C-enriched sample. All modes of the Z-center are visible. The inset displays the isotope splitting of the modes Z_D and Z_C as well as the three-fold splitting of the highest HT3-mode. (c) The centers Z, U, HT3 and HT4 in a sample with natural isotope abundance. The overlap of the ZPL of HT4 and the high-energy mode of HT3 is clearly visible, as well as the narrow separation between the lower-energy mode of HT3 and the ZPL of the U-center.
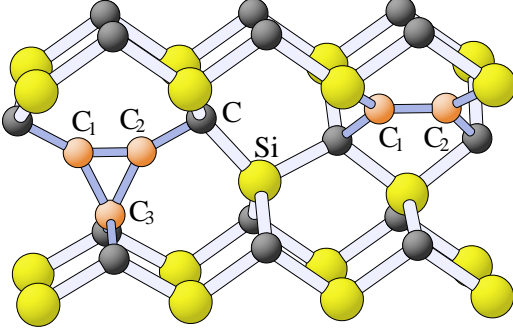

FIG. 2: The tri-carbon antisite $(C_3)_{Si}$ (left) and the carbon di-interstitial $(C_2)_{Hex}$ (right) in 3C-SiC.

towards each other, so that a configuration similar to $(C_2)_{Hex}$ in 3C-SiC forms. All these defects are neutral for practically all positions of the Fermi-level.

Both defects show a distinct vibrational pattern. The frequencies of the LVM's in 3C- and 4H-SiC are listed in Table II. Since the defects possess mirror symmetry (which is in 4H-SiC limited to the defect molecule), the modes are marked as symmetric (g) or antisymmetric (u) vibrations. This is important for PL experiments, since the bound exciton mostly interacts with a symmetric but not with an antisymmetric vibration.[11] It is clearly visible from Table II that the LVM's of the defects are practically independent of the polytype and the involved cubic or hexagonal sites. We therefore expect that our results for the 3C and 4H polytypes are transferrable to 6H-SiC.

The di-interstitial possesses four LVM's above the SiC bulk phonon spectrum. The LVM's at $160\,\mathrm{mev}$ and $190\,\mathrm{meV}$ are symmetric vibrations (cf. Table II). The highest mode shows a clear three-fold isotope splitting, while the lower-energy modes show a complex broaden-

ing or splitting (cf. Fig. 3a). The relative height of the peaks within a mode results from the various possibilities of substituting a defect's atom with ^{13}C assuming an enrichment of 30%. The peak heights of different modes are independent and cannot be compared. Considering the two symmetric modes of $(C_2)_{Hex}$, the spectrum is similar to that of the Z- and the HT5-center. Besides, as in 4H-SiC various different defect configurations involving the two cubic and the hexagonal sites are possible in 6H-SiC, allowing for different exciton binding energies (and therefore different ZPL's) with comparable phonon replicas. However, the calculated values are systematically about $10\,\mathrm{meV}$ lower than the measured frequencies. This finding is especially noteworthy since the LDA tends to overestimate the calculated frequencies.

The tricarbon antisite $(C_3)_{Si}$ has five LVM's above the bulk phonon spectrum. Symmetric modes are the mode 5 at $250\,\mathrm{meV}$ and the mode 3 at $150\,\mathrm{meV}$. All other modes are antisymmetric (cf. Table II). The isotope splitting of the defect in 3C- and 4H-SiC is displayed in Fig. 3b alongside the measured frequencies for the U-center (the centers HT3 and HT4 have similar phonon replicas, cf. Table I). The mode 5 shows a clear three-fold isotope splitting as one would expect for a simple carbon dumbbell vibration. This simple pattern results from the localization of the vibration onto the atoms C_1 and C_2 of the triangular defect, whereas the neighboring atoms are practically not involved. In contrast, the neighbor atoms do participate in the vibration of the mode 3. Consequently, this mode exhibits a significant broadening due to the ^{13}C-enrichment. The measured values of the U-, HT3-, and HT4-centers are in excellent agreement with the calculated absolute values of the symmetric modes of $(C_3)_{Si}$. The isotope splitting of the centers is also well reproduced. The antisymmetric modes should be suppressed in photoluminescence as discussed above. In 6H-

TABLE II: Calculated LVM's in meV of the carbon di-interstitials $(C_2)_{Hex}$ and the tri-carbon antisite $(C_3)_{Si}$. In 4H-SiC, further di-interstitials exist with similar geometrical configuration and similar vibrational properties (see Ref. 3). The letters g and u denote symmetric and antisymmetric vibrations, respectively.

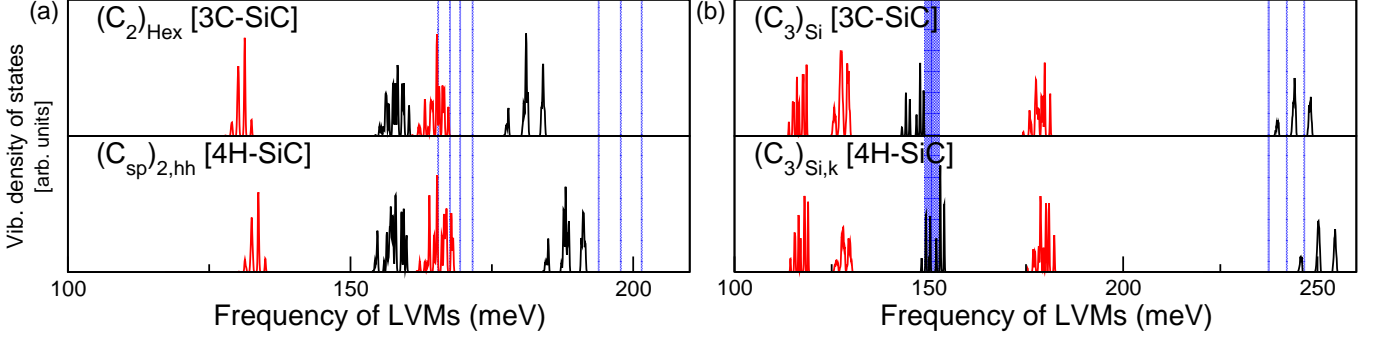| LVM	$(C_2)_{Hex}$ (3C)	$(C_{sp})_{2,hk,cub}$ (4H)	$(C_{sp})_{2,hh}$ (4H)	$(C_3)_{Si}$ (3C)	$(C_3)_{Si,k}$ (4H)	$(C_3)_{Si,h}$ (4H)
1	132.5 (u)	128.0 (u)	134.9 (u)	118.6 (u)	119.0 (u)	119.0 (u)
2	160.4 (g)	161.3 (g)	159.9 (g)	129.8 (u)	130.2 (u)	130.5 (u)
3	167.3 (u)	167.1 (u)	168.1 (u)	148.7 (g)	154.0 (g)	154.2 (g)
4	184.3 (g)	189.1 (g)	191.5 (g)	181.3 (u)	182.3 (u)	182.6 (u)
5				248.5 (g)	254.9 (g)	255.7 (g)

FIG. 3: (Color online) Calculated LVM's of (a) the carbon di-interstitials and (b) the tri-carbon antisite in 3C and 4H-SiC with a ^{13}C-enrichment of 30%. The black peaks indicate symmetric modes, the red (gray) peaks are antisymmetric vibrations. The phonon replicas of the Z-center (a) and the U-center (b) including isotope shifts are indicated by the blue (shaded) lines.

SiC the defect can be located at the cubic sites k_1 and k_2 or at the hexagonal site h, providing three different defect configurations. As observed for 4H-SiC, the difference of the vibrational patterns for the different sites shall be negligible. Thus we believe that $(C_3)_{Si}$ should be a good model for the centers U, HT3 and HT4 in 6H-SiC.

In conclusion, we presented thermally stable photoluminescence centers in 6H-SiC with localized vibrational modes up to 250 meV. All centers show a clear three-fold isotope splitting of the highest mode with the frequency ratio typical for a carbon-carbon dumbbell vibration. Based on the vibrational spectra obtained from *ab initio* calculations, the di-interstitial $(C_2)_{Hex}$ is considered as a model for the centers Z and HT5, although a systematic frequency shift of 10 meV is observed. The results obtained for the tri-carbon antisite $(C_3)_{Si}$ are in excellent agreement with the U-, HT3-, and HT4-centers. This identification demonstrates the possibility of carbon aggregates predicted earlier theoretically.[2,3,4]

[*] Electronic address: Mattausch@physik.uni-erlangen.de

[†] Electronic address: J.W.Steeds@bristol.ac.uk

[1] L. Patrick and W. J. Choyke, J. Phys. Chem. Solids **34**, 565 (1973); F. H. C. Carlsson, S. G. Sridhara, A. Hallén, J. P. Bergman, and E. Janzén, Mater. Sci. Forum **433-436**, 345 (2003).

[2] A. Mattausch, M. Bockstedte, and O. Pankratov, Phys. Rev. B **69**, 045322 (2004), cond-mat/0309112.

[3] A. Mattausch, M. Bockstedte, and O. Pankratov, Phys. Rev. B **70**, 235211 (2004), cond-mat/0409318.

[4] A. Gali, P. Deák, P. Ordejón, N. T. Son, E. Janzén, and W. J. Choyke, Phys. Rev. B **68**, 125201 (2003).

[5] G. A. Evans, J. W. Steeds, L. Ley, M. Hundhausen, N. Schulze, and G. Pensl, Phys. Rev. B **66**, 035204 (2002).

[6] M. Bockstedte, A. Mattausch, and O. Pankratov, Phys. Rev. B **69**, 235202 (2004), cond-mat/0309703.

[7] T. Egilsson, J. P. Bergman, I. G. Ivanov, A. Henry, and E. Janzén, Phys. Rev. B **59**, 1956 (1999); T. A. G. Eberlein, C. J. Fall, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **65**, 184108 (2002).

[8] J. W. Steeds, G. A. Evans, L. R. Danks, S. Furkert, W. Voegeli, M. M. Ismail, and F. Carosella, Diam. Rel. Mat. **11**, 1923 (2002).

[9] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comp. Phys. Commun. **107**, 187 (1997).

[10] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[11] M. E. Pistol and B. Monemar, Phys. Rev. B **33**, 7006 (1986).